

COATING COMPOSITION AND A PROCESS FOR ITS PREPARATION

CROSS REFERENCE TO RELATED PATENT APPLICATION

The present patent application claims the right of priority under 35 U.S.C. §119 (a)-(d) of German Patent Application No. 102 45 729.8, filed October 1, 2002.

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FIELD OF THE INVENTION

The present invention relates to a process for the preparation of coating compositions and the compositions which can be obtained by this process. The invention furthermore relates to layer systems comprising a substrate  
10 (S), a scratch-resistant layer (SR) and a top layer (T) prepared from the coating composition according to the invention, and to a process for the preparation of these layer systems.

BACKGROUND OF THE INVENTION

15 With the aid of sol-gel processes it is possible to prepare materials which are suitable as coatings from alkoxides such as aluminium propanolate or butanolate using modified alkoxysilanes. Typically, sol-gel processes are characterised in that a mixture of the starting components is reacted by a hydrolysis and condensation process to form a viscous liquid phase. An  
20 organically modified inorganic base matrix which has an increased surface hardness compared with conventional organic polymers is formed by this synthesis method. However, an important disadvantage of sol gel processes relates to the high reactivity of the aluminium-containing components, which results in reduced storage stability (pot life) of the  
25 reactant composition.

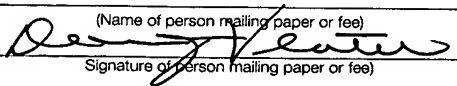
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Compared with inorganic materials, the layers obtained by sol-gel processes are relatively soft. Even though the inorganic contents of the system provide a high level of crosslinking, the reason for the reduced layer hardness is believed to be due to the small size of the inorganic materials in the system, which reduces the mechanical properties (e.g., hardness and abrasion resistance) of the layers. By the use of filler-containing polymers, the favourable mechanical properties of the inorganic contents can be more fully utilized, since in this case the filler provides inorganic particles having sizes of several micrometres.

However, the transparency of the materials is typically lost, and optical uses are typically not possible. The use of small particles of SiO<sub>2</sub> (e.g., Aerosils® particles) for the preparation of transparent layers having increased abrasion resistance is possible, but at the low concentrations that are typically employed the abrasion resistance of the layers is unfortunately similar to those of the above-mentioned system. The upper limit of the amount of filler is determined in part by the high surface reactivity of the small particles, which results undesirably in the formation of agglomerations or in increases in viscosity.

DE 199 52 040 A1 discloses substrates with an abrasion-resistant diffusion barrier layer system, wherein the diffusion barrier layer system comprises a hard base layer based on hydrolysable epoxysilanes and a top layer arranged on top. The top layer is obtained by application of a coating sol of tetraethoxysilane (TEOS) and glycidyloxypropyl-trimethoxysilane (GPTS) and curing thereof at a temperature of < 110°C. The coating sol is prepared by subjecting TEOS to prehydrolysis and condensation with ethanol as the solvent in HCl-acid aqueous solution. GPTS is then stirred into the TEOS prehydrolysed in this way and the sol is stirred for 5 hours at 50°C. A disadvantage of the coating sol described in this publication is its low storage stability (pot life), as a consequence of which the coating sol must be further processed within a few days after its preparation. A disadvantage of the diffusion barrier layer systems

described in this publication is furthermore that these have results according to the Taber abrasion test which are unsatisfactory for use in automobile glazing.

- 5 DE 43 38 361 A1 describes coating compositions which comprise silicon compounds containing epoxide groups, nanoscale oxides or oxide hydrates of Si, Al, B or transition metals, where boehmite is preferred in particular, surfactants and aromatic polyols. The compositions may additionally comprise Lewis bases and alcoholates of titanium, zirconium  
10 or aluminium. The compositions are prepared by the sol-gel process, by prehydrolysing GPTS and TEOS together in HCl-acid solution, not more than about 0.5 mol of water being employed per mol of hydrolysable group. After the hydrolysis has taken place, boehmite sol is added to the composition, while cooling with ice. The coating compositions are used for  
15 the preparation of scratch-resistant layers. Over-coating of the scratch-resistant layer with a further top layer is not described in this publication.

#### SUMMARY OF THE INVENTION

- The invention is based on the object of providing an organically modified  
20 inorganic system which, in its hardness, is significantly superior to that of the materials described in the prior art, and has a high optical transparency. A further object of the invention is to provide for the preparation of stable intermediate products which can be used as coatings, which have properties that are substantially constant over time.  
25 In addition, another object of the invention, is to provide intermediate products which allow for modification of the physical and chemical surface properties of a coating, such as hydrophilicity / hydrophobicity and correspondingly oleophilicity / oleophobicity surface properties.

The present invention is based on the object of providing a composition with an even further improved scratch resistance, adhesion, paint viscosity and elasticity, which has a lower tendency towards gelling and hazing compared with the compositions of the prior art.

5

In accordance with the present invention, there is provided a process of preparing a coating composition comprising forming a hydrolysis product by hydrolysing:

- (a) at least one compound represented by general formula I,

10



wherein M is an element selected from the group consisting of Si, Ti, Zr, Sn, Ce, Al, B, VO, In and Zn, R' represents a hydrolysable radical, and m is an integer from 2 to 4; and

15

- (b) optionally at least one compound represented by general formula II,



20

wherein the radicals R' and R are the same or different, R' is as defined above, R represents a group selected from an alkyl group, an alkenyl group, an aryl group, a hydrocarbon group with at least one halogen group, an epoxide group, a glycidyloxy group, an amino group, a mercapto group, a methacryloxy group and a cyano group, and a and b independently of one another have a value from 1 to 3, provided that the sum of a and b is four,

25

wherein the hydrolysis occurs in the presence of at least 0.6 moles of water for every mole of hydrolysable radical R'.

30

Unless otherwise indicated, all numbers or expressions, such as those expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are understood as modified in all instances by the term "about."

5

#### DETAILED DESCRIPTION OF THE INVENTION

It has been found, surprisingly, that by the joint hydrolysis of the compounds of the formulae I and II envisaged in the process according to the invention, the storage stability (pot life) of the composition is improved considerably.

10

In contrast to the doctrine of DE 43 38 361 A1, the hydrolysis is carried out in the presence of at least 0.6 mol of water, in particular 0.8 to 2.0 mol of water, based on 1 mol of hydrolysable radicals R'. According to a preferred embodiment of the invention, a complete hydrolysis is carried out by using at least an equimolar amount of water, based on the hydrolysable radicals.

15

The compounds of the formulae I and II can be employed in any desired amounts. The compound of the formula II is preferably employed in an amount of less than 0.7 mol, in particular less than 0.5 mol, based on 1 mol of the compound of the formula I.

20

The hydrolysis is preferably carried out in the presence of acids, in particular aqueous hydrochloric acid. A pH of the reaction mixture of 2.0 to 5.0 is particularly suitable.

25

The hydrolysis reaction proceeds slightly exothermically and is preferably assisted by heating to 30 to 40°C. When the hydrolysis has taken place, the reaction product is preferably cooled to room temperature and stirred for some time, in particular 1 to 3 hours, at room temperature. The coating composition obtained is preferably stored at temperatures of <10°C, in particular at a temperature of about 4°C.

30

All the temperature data include a deviation of  $\pm 2^{\circ}\text{C}$ . Room temperature is understood as meaning a temperature of 20 to  $23^{\circ}\text{C}$ .

5 The over-coating sol is prepared from 100 parts of a compound of the formula I and/or of a hydrolysis product therefrom and of a compound of the formula II and/or of a hydrolysis product therefrom, the amount of the compound II, based on the 100 parts of the compound I, being less than 100 parts, preferably less than 70 parts, in particular less than 50 parts or also being omitted completely. The ready-to-apply top layer coating  
10 composition preferably has a solids content of 0.2 to 5 wt.%, in particular 0.5 to 3 wt.%.

The compound of the formula I is preferably a compound

15



wherein M represents a)  $\text{Si}^{+4}$ ,  $\text{Ti}^{+4}$ ,  $\text{Zr}^{+4}$ ,  $\text{Sn}^{+4}$  or  $\text{Ce}^{+4}$  or b)  $\text{Al}^{+3}$ ,  $\text{B}^{+3}$ ,  $\text{VO}^{+3}$  or  $\text{In}^{+3}$  or c)  $\text{Zn}^{+2}$ , R represents a hydrolysable radical and m is 4 in the case of tetravalent elements M [case a)], 3 in the case of trivalent  
20 elements or compounds M [case b)], and 2 in the case of divalent elements [case c)]. Preferred elements for M are  $\text{Si}^{+4}$ ,  $\text{Ti}^{+4}$ ,  $\text{Ce}^{+4}$  and  $\text{Al}^{+3}$ , and  $\text{Si}^{+4}$  is particularly preferred.

Examples of the hydrolysable radicals are halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular  $\text{C}_{1-4}$ -alkoxy, such as e.g. methoxy, ethoxy, n-propoxy, i-propoxy and n-butoxy, i-butoxy, sec-butoxy or tert-butoxy), aryloxy (in particular  $\text{C}_{6-10}$ -aryloxy, e.g. phenoxy), acyloxy (in particular  $\text{C}_{1-4}$ -acyloxy, such as e.g. acetoxymethoxy and propionylmethoxy) and alkylcarbonyl (e.g. acetyl). Particularly preferred hydrolysable radicals are  
30 alkoxy groups, in particular methoxy and ethoxy.

Specific examples of compounds of the formula I which can be employed are given in the following, but these are not intended to represent a limitation of the compounds of the formula I which can be employed.

- 5     $\text{Si}(\text{OCH}_3)_4$ ,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Si}(\text{O-n- or i-C}_3\text{H}_7)_4$ ,  
       $\text{Si}(\text{OC}_4\text{H}_9)_4$ ,  $\text{SiCl}_4$ ,  $\text{HSiCl}_3$ ,  $\text{Si}(\text{OOCCH}_3)_4$ ,
- $\text{Al}(\text{OCH}_3)_3$ ,  $\text{Al}(\text{OC}_2\text{H}_5)_3$ ,  $\text{Al}(\text{O-n-C}_3\text{H}_7)_3$ ,  
       $\text{Al}(\text{O-i-C}_3\text{H}_7)_3$ ,  $\text{Al}(\text{OC}_4\text{H}_9)_3$ ,  $\text{Al}(\text{O-i-C}_4\text{H}_9)_3$ ,
- 10    $\text{Al}(\text{O-sec-C}_4\text{H}_9)_3$ ,  $\text{AlCl}_3$ ,  $\text{AlCl}(\text{OH})_2$ ,  $\text{Al}(\text{OC}_2\text{H}_4\text{OC}_4\text{H}_9)_3$ ,
- $\text{TiCl}_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ ,  
       $\text{Ti}(\text{O-i-C}_3\text{H}_7)_4$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ti}(\text{2-ethylhexoxy})_4$ ;
- 15    $\text{ZrCl}_4$ ,  $\text{Zr}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Zr}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{O-i-C}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ,
- $\text{ZrOCl}_2$ ,  $\text{Zr}(\text{2-ethylhexoxy})_4$
- and Zr compounds which contain complexing radicals, such as e.g.
- 20    $\beta$ -diketone and methacryl radicals,
- $\text{BCl}_3$ ,  $\text{B}(\text{OCH}_3)_3$ ,  $\text{B}(\text{OC}_2\text{H}_5)_3$ ,
- $\text{SnCl}_4$ ,  $\text{Sn}(\text{OCH}_3)_4$ ,
- 25    $\text{Sn}(\text{OC}_2\text{H}_5)_4$ ,
- $\text{VOCl}_3$ ,  $\text{VO}(\text{OCH}_3)_3$ ,
- $\text{Ce}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ce}(\text{OC}_3\text{H}_7)_4$ ,  $\text{Ce}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Ce}(\text{O-i-C}_3\text{H}_7)_4$ ,  $\text{Ce}(\text{2-ethylhexoxy})_4$ ,
- 30    $\text{Ce}(\text{SO}_4)_2$ ,  $\text{Ce}(\text{ClO}_4)_4$ ,  $\text{CeF}_4$ ,  $\text{CeCl}_4$ ,  $\text{CeAc}_4$ ,

$\text{In}(\text{CH}_3\text{COO})_3$ ,  $\text{In}[\text{CH}_3\text{COCH} = \text{C}(\text{O}-)\text{CH}_3]_3$ ,

$\text{InBr}_3$ ,  $[(\text{CH}_3)_3\text{CO}]_3\text{In}$ ,  $\text{InCl}_3$ ,  $\text{InF}_3$ ,

$[(\text{CH}_3)_2\text{CHO}]_3\text{In}$ ,  $\text{InI}_3$ ,  $\text{In}(\text{NO}_3)_3$ ,  $\text{In}(\text{ClO}_4)_3$ ,  $\text{In}_2(\text{SO}_4)_3$ ,  $\text{In}_2\text{S}_3$ ,

5  $(\text{CH}_3\text{COO})_2\text{Zn}$ ,  $[\text{CH}_3\text{COCH} = \text{C}(\text{O}-)\text{CH}_3]_2\text{Zn}$ ,

$\text{ZnBr}_2$ ,  $\text{ZnCO}_3 \cdot 2 \text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnCl}_2$ ,

zinc citrate,  $\text{ZnF}_2$ ,  $\text{ZnI}_2$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ .

10 Compounds  $\text{SiR}_4$ , wherein the radicals R can be identical or different and represent a hydrolysable group, preferably an alkoxy group having 1 to 4 carbon atoms, in particular methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, sec-butoxy or tert-butoxy, are particularly preferably employed.

15 A tetraalkoxysilane, in particular tetraethoxysilane (TEOS), is very particularly preferred.

The compound of the formula II is preferably a compound

20  $\text{R}_b\text{SiR}'_a$ , (II)

wherein the radicals R and R' are identical or different (preferably identical), the R' represent a hydrolysable group (preferably  $\text{C}_{1-4}$ -alkoxy, and in particular methoxy and ethoxy) and the R represent an alkyl (preferably  $\text{C}_1\text{-C}_8$ ) group, an alkenyl (preferably  $\text{C}_2\text{-C}_8$ ) group, an aryl (preferably  $\text{C}_6\text{-C}_{10}$ ) group or a hydrocarbon group (preferably  $\text{C}_1\text{-C}_{20}$ ) with one or more halogen groups, an epoxide group, a glycidyloxy group, an amino group, a mercapto group, a methacryloxy group or a cyano group.

30 In formula II, subscript (a) can assume the values 1 to 3, and subscript (b) can also assume the values 1 to 3, provided that the sum of (a + b) is four.



Examples of compounds of the formula II include, but are not limited to:

- trialkoxysilanes, triacyloxysilanes and triphenoxysilanes, those such as methyltrimethoxysilane, methyltriethoxysilane,
- 5 methyltrimethoxyethoxysilane, methyltriacetoxysilane, methyltributoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, vinyltrimethoxyethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane, phenyltriacetoxysilane,  $\gamma$ -chloropropyltrimethoxysilane,
- 10  $\gamma$ -chloropropyltriethoxysilane,  $\gamma$ -chloropropyltriacetoxysilane, 3,3,3-trifluoropropyltrimethoxysilane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane,  $\gamma$ -mercaptopropyltriethoxysilane, N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane,
- 15  $\beta$ -cyanoethyltriethoxysilane, methyltriphenoxysilane, chloromethyltrimethoxysilane, chloromethyltriethoxysilane, glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane,  $\alpha$ -glycidoxyethyltrimethoxysilane,  $\alpha$ -glycidoxyethyltriethoxysilane,  $\beta$ -glycidoxyethyltrimethoxysilane,  $\beta$ -glycidoxyethyltriethoxysilane,
- 20  $\alpha$ -glycidoxypropyltrimethoxysilane,  $\alpha$ -glycidoxypropyltriethoxysilane,  $\beta$ -glycidoxypropyltrimethoxysilane,  $\beta$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltriethoxysilane,  $\gamma$ -glycidoxypropyltripropoxysilane,  $\gamma$ -glycidoxypropyltributoxysilane,  $\gamma$ -glycidoxypropyltrimethoxyethoxysilane,
- 25  $\gamma$ -glycidoxypropyltriphenoxysilane,  $\alpha$ -glycidoxybutyltrimethoxysilane,  $\alpha$ -glycidoxybutyltriethoxysilane,  $\beta$ -glycidoxybutyltrimethoxysilane,  $\beta$ -glycidoxybutyltriethoxysilane,  $\gamma$ -glycidoxybutyltrimethoxysilane,  $\gamma$ -glycidoxybutyltriethoxysilane,  $\delta$ -glycidoxybutyltrimethoxysilane,  $\delta$ -glycidoxybutyltriethoxysilane,
- 30 (3,4-epoxycyclohexyl)methyltrimethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane,

- $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltripropoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltributoxysilane,  
5  $\beta$ -(3,4-epoxycyclohexyl)ethyldimethoxyethoxysilane,  
 $\beta$ -(3,4-epoxycyclohexyl)ethyltriphenoxysilane,  
 $\gamma$ -(3,4-epoxycyclohexyl)propyltrimethoxysilane,  
 $\gamma$ -(3,4-epoxycyclohexyl)propyltrimethoxysilane,  
 $\delta$ -(3,4-epoxycyclohexyl)butyltrimethoxysilane;  
10  $\delta$ -(3,4-epoxycyclohexyl)butyltriethoxysilane and hydrolysis products  
therefrom, and dialkoxysilanes and diacyloxysilanes, such as e.g.  
dimethyldimethoxysilane, phenylmethyldimethoxysilane,  
dimethyldiethoxysilane, phenylmethyldiethoxysilane,  
 $\gamma$ -chloropropylmethyldimethoxysilane,  $\gamma$ -chloropropylmethyldiethoxysilane,  
15 dimethyldiacetoxysilane,  $\gamma$ -methacryloxypropylmethyldimethoxysilane,  
 $\gamma$ -methacryloxypropylmethyldiethoxysilane,  
 $\gamma$ -mercaptopropylmethyldimethoxysilane,  
 $\gamma$ -mercaptopropylmethyldiethoxysilane,  
 $\gamma$ -aminopropylmethyldimethoxysilane,  
20  $\gamma$ -aminopropylmethyldiethoxysilane, methylvinylmethyldimethoxysilane, methyl-  
vinylmethyldiethoxysilane, glycidoxymethylmethyldimethoxysilane,  
glycidoxymethylmethyldiethoxysilane,  
 $\alpha$ -glycidoxyethylmethyldimethoxysilane,  
 $\alpha$ -glycidoxyethylmethyldiethoxysilane,  
25  $\beta$ -glycidoxyethylmethyldimethoxysilane,  
 $\beta$ -glycidoxyethylmethyldiethoxysilane,  
 $\alpha$ -glycidoxypropylmethyldimethoxysilane,  
 $\alpha$ -glycidoxypropylmethyldiethoxysilane,  
 $\beta$ -glycidoxypropylmethyldimethoxysilane,  
30  $\beta$ -glycidoxypropylmethyldiethoxysilane,

- $\gamma$ -glycidoxypropylmethyldimethoxysilane,  
 $\gamma$ -glycidoxypropylmethyldiethoxysilane,  
 $\gamma$ -glycidoxypropylmethyldipropoxysilane,  
 $\gamma$ -glycidoxypropylmethyldibutoxysilane,  
5  $\gamma$ -glycidoxypropylmethyldimethoxyethoxysilane,  
 $\gamma$ -glycidoxypropylmethyldiphenoxysilane,  
 $\gamma$ -glycidoxypropylethyldimethoxysilane,  
 $\gamma$ -glycidoxypropylethyldiethoxysilane,  
 $\gamma$ -glycidoxypropylethyldipropoxysilane,  
10  $\gamma$ -glycidoxypropylvinyl dimethoxysilane,  
 $\gamma$ -glycidoxypropylvinyl diethoxysilane,  
 $\gamma$ -glycidoxypropylphenyldimethoxysilane,  
 $\gamma$ -glycidoxypropylphenyldiethoxysilane, and products and hydrolysis  
products therefrom.  
15
- The examples of formula II may be used individually or as a mixture of two or more.
- Preferred compounds of the formula II are methyltrialkoxysilane, dimethyl-  
20 dialkoxysilane, glycidyloxypropyltrialkoxysilane and/or methacryloxypropyl-  
trimethoxysilane. Particularly preferred compounds of the formula II are  
glycidyloxypropyltrimethoxysilane (GPTS), methyltriethoxysilane (MTS)  
and/or methacryloxypropyltrimethoxysilane (MPTS).
- 25 Water and inert solvents or solvent mixtures can optionally be added at  
any desired stage of the preparation, in particular during the hydrolysis, in  
order to adjust the rheological properties of the compositions. These  
solvents are preferably alcohols which are liquid at room temperature,  
which are moreover also formed during the hydrolysis of the alkoxides  
30 preferably employed. Particularly preferred alcohols are C<sub>1-8</sub>-alcohols, in  
particular methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol,

tert-butanol, n-pentanol, i-pentanol, n-hexanol and n-octanol. C<sub>1-6</sub>-Glycol ethers, in particular n-butoxyethanol, are also preferred. Isopropanol, ethanol, butanol and/or water is particularly suitable as the solvent.

- 5 The compositions can furthermore comprise conventional additives, such as e.g. dyestuffs, flow control agents, UV stabilizers, IR stabilizers, photoinitiators, photosensitizers (if photochemical curing of the composition is intended) and/or thermal polymerization catalysts. Flow control agents are, in particular, those based on polyether-modified
- 10 polydimethylsiloxanes. It has proved particularly advantageous if the coating compositions comprise flow control agents in an amount of about 0.005 to 2 wt. %.

- The coating composition prepared in this way can be employed for coating
- 15 the most diverse substrates. The choice of the substrate materials for coating is not limited. The compositions are preferably suitable for coating wood, textiles, paper, stoneware, metals, glass, ceramic and plastics, and here in particular for coating thermoplastics, such as are described in Becker/Braun, Kunststoffaschenbuch, Carl Hanser Verlag, Munich,
- 20 Vienna 1992. The compositions are very particularly suitable for coating transparent thermoplastics, and preferably polycarbonates. In particular, spectacle lenses, optical lenses, automobile windows and sheets can be coated with the compositions obtained according to the invention.

- 25 The application to the substrate is carried out by standard coating processes, such as e.g. dipping, flow-coating, spreading, brushing, knife-coating, rolling, spraying, falling film application, spin-coating and whirler-coating.

- 30 Curing of the coated substrate is carried out optionally after prior surface-drying at room temperature. The curing is preferably carried out by means of heat at temperatures in the range from 50 to 200°C, in particular 70 to

180°C and particularly preferably 90 to 150°C. Under these conditions the curing time should be 30 to 200 minutes, preferably 45 to 120 minutes.

The layer thickness of the cured top layer should be 0.05 to 5 µm, preferably 0.1 to 3 µm.

5

If unsaturated compounds and photoinitiators are present, the curing can also be carried out by irradiation, which is optionally followed by after-curing by means of heat.

- 10 The coating compositions prepared by the process according to the invention are suitable in particular for the preparation of top layers (D) in scratch-resistant coating systems. The coating compositions prepared by the process according to the invention are particularly suitable for application to scratch-resistant layers (SR) based on hydrolysable silanes
- 15 with epoxide groups. Preferred scratch-resistant layers (SR) are those which are obtainable by curing of a coating composition comprising a polycondensate, prepared by the sol-gel process, based on at least one silane which has an epoxide group on a non-hydrolysable substituent and optionally a curing catalyst chosen from Lewis bases and alcoholates of
- 20 titanium, zirconium or aluminium. The preparation and properties of such scratch-resistant layers (SR) are described, for example, in DE 43 38 361 A1.

Scratch-resistant layers (SR) which are over-coated with the coating

25 composition prepared by the process according to the invention are preferably those which are prepared from a coating composition comprising

- a silicon compound (A) with at least one radical R which cannot be
- 30 split off by hydrolysis, is bonded directly to Si and contains an epoxide group,

- particulate materials (B),
  - a hydrolysable compound (C) of Si, Ti, Zr, B, Sn or V and preferably additionally
- 5     - a hydrolysable compound (D) of Ti, Zr or Al.

Such coating compositions result in highly scratch-resistant coatings which adhere particularly well to the material.

- 10    The compounds (A) to (D) are explained in more detail in the following.  
The compounds (A) to (D) can be contained not only in the composition for the scratch-resistant layer (SR), but also as additional component(s) in the composition for the top layer (T)

15    **Silicon compound (A)**

- The silicon compound (A) is a silicon compound which has 2 or 3, preferably 3, hydrolysable radicals and one or 2, preferably one, non-hydrolysable radical. The only or at least one of the two non-hydrolysable radicals has an epoxide group.
- 20

- Examples of the hydrolysable radicals are halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular C<sub>1-4</sub>-alkoxy, such as e.g. methoxy, ethoxy, n-propoxy, i-propoxy and n-butoxy, i-butoxy, sec-butoxy and tert-butoxy), aryloxy (in particular C<sub>6-10</sub>-aryloxy, e.g. phenoxy), acyloxy (in particular C<sub>1-4</sub>-acyloxy, such as e.g. acetoxy and propionyloxy) and alkylcarbonyl (e.g. acetyl). Particularly preferred hydrolysable radicals are alkoxy groups, in particular methoxy and ethoxy.
- 25

- 30    Examples of non-hydrolysable radicals without an epoxide group are hydrogen, alkyl, in particular C<sub>1-4</sub>-alkyl (such as e.g. methyl, ethyl, propyl and butyl), alkenyl (in particular C<sub>2-4</sub>-alkenyl, such as e.g. vinyl, 1-propenyl,

- 2-propenyl and butenyl), alkynyl (in particular C<sub>2-4</sub>-alkynyl, such as e.g. acetylenyl and propargyl) and aryl, in particular C<sub>6-10</sub>-aryl, such as e.g. phenyl and naphthyl), it being possible for the groups just mentioned optionally to contain one or more substituents, such as e.g. halogen and alkoxy. Methacryl and methacryloxypropyl radicals may also be mentioned in this connection.

Examples of non-hydrolysable radicals with an epoxide group are, in particular, those which have a glycidyl or glycidyloxy group.

10

Examples of silicon compounds (A) which can be employed according to the invention may be found, for example, on pages 8 and 9 of EP-A-195 493.

- 15 Silicon compounds (A) which are particularly preferred according to the invention are those of the general formula



- 20 in which the radicals R are identical or different (preferably identical) and represent a hydrolysable group (preferably C<sub>1-4</sub>-alkoxy and in particular methoxy and ethoxy) and R' represent a a glycidyl or glycidyloxy-(C<sub>1-20</sub>)-alkylene radical, in particular  $\beta$ -glycidyloxyethyl,  $\gamma$ -glycidyloxypropyl,  $\delta$ -glycidyloxybutyl,  $\epsilon$ -glycidyloxypentyl,  $\omega$ -glycidyloxyhexyl,  $\omega$ -glycidyloxyoctyl,  $\omega$ -glycidyloxynonyl,  $\omega$ -glycidyloxydecyl,  $\omega$ -glycidyloxydodecyl and 2-(3,4-Epoxy cyclohexyl)-ethyl.

- 30  $\gamma$ -Glycidyloxy-propyltrimethoxysilane (abbreviated to GPTS in the following) is particularly preferably employed according to the invention because of its easy accessibility.

**Particulate materials (B),**

The particulate materials (B) may be an oxide, oxide hydrate, nitride or carbide of Si, Al and B and of transition metals, preferably Ti, Zr and Ce, with a particle size in the range from 1 to 100, preferably 2 to 50 nm and particularly preferably 5 to 20 nm and mixtures thereof. These materials can be employed in the form of a powder, but are preferably used in the form of a sol (in particular an acid-stabilized sol). Preferred particulate materials are boehmite,  $\text{SiO}_2$ ,  $\text{CeO}_2$ ,  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$  and  $\text{TiO}_2$ . Nanoscale boehmite particles are particularly preferred. The particulate materials are commercially obtainable in the form of powders, and the preparation of (acid-stabilized) sols therefrom is also known in the prior art. Reference can moreover be made in this context to the preparation examples described below. The principle of stabilization of nanoscale titanium nitride by means of guanidinepropionic acid is described e.g. in German Patent Application DE-43 34 639 A1.

Boehmite sol with a pH in the range from 2.5 to 3.5, preferably 2.8 to 3.2, which can be obtained, for example, by suspending boehmite powder in dilute HCl, is particularly preferably employed.

The variation of the nanoscale particles is as a rule accompanied by a variation in the refractive index of the corresponding materials. Thus, for example, the replacement of boehmite particles by  $\text{CeO}_2$ ,  $\text{ZrO}_2$  or  $\text{TiO}_2$  particles leads to materials with higher refractive indices, the refractive index resulting additively from the volume of the component of high refractive index and the matrix in accordance with the Lorentz-Lorenz equation.

As mentioned, cerium dioxide can be employed as the particulate material. This preferably has a particle size in the range from 1 to 100, preferably 2 to 50 nm and particularly preferably 5 to 20 nm. This material can be employed in the form of a powder, but is preferably used in the form of a



sol (in particular an acid-stabilized sol). Particulate cerium oxide is commercially obtainable in the form of sols and powders, and the preparation of (acid-stabilized) sols therefrom is also known in the prior art.

- 5 Compound (B) is preferably employed in the composition for the scratch-resistant layer (SR) in an amount of 3 to 60 wt.%, based on the solids content of the coating composition for the scratch-resistant layer (SR).

### Hydrolysable compounds (C)

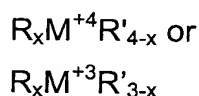
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In addition to the silicon compounds (A), other hydrolysable compounds of elements from the group consisting of Si, Ti, Zr, Al, B, Sn and V are also used for the preparation of the scratch-resistant layer coating composition and are preferably hydrolysed with the silicon compound(s) (A).

15

The compound (C) is a compound of Si, Ti, Zr, B, Sn and V of the general formula

20



25

wherein M represents a)  $Si^{+4}$ ,  $Ti^{+4}$ ,  $Zr^{+4}$  or  $Sn^{+4}$ , or b)  $Al^{+3}$ ,  $B^{+3}$  or  $(VO)^{+3}$ , R represents a hydrolysable radical, R' represents a non-hydrolysable radical and x can be 1 to 4 in the case of tetravalent metal atoms M (case a)) and 1 to 3 in the case of trivalent metal atoms M (case b)). If several radicals R and/or R' are present in a compound (C), these can in each case be identical or different. Preferably, x is greater than 1. That is to say the compound (C) contains at least one, preferably several, hydrolysable radicals.

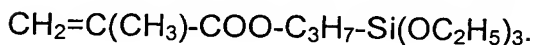
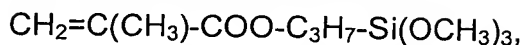
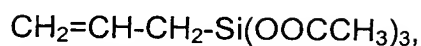
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Examples of the hydrolysable radicals are halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular C<sub>1-4</sub>-alkoxy, such as e.g. methoxy, ethoxy, n-propoxy, i-propoxy and n-butoxy, i-butoxy, sec-butoxy or tert-butoxy), aryloxy (in particular C<sub>6-10</sub>-aryloxy, e.g. phenoxy), acyloxy (in particular C<sub>1-4</sub>-acyloxy, such as e.g. acetoxy and propionyloxy) and alkylcarbonyl (e.g. acetyl). Particularly preferred hydrolysable radicals are alkoxy groups, in particular methoxy and ethoxy.

Examples of non-hydrolysable radicals are hydrogen, alkyl, in particular C<sub>1-4</sub>-alkyl (such as e.g. methyl, ethyl, propyl and n-butyl, i-butyl, sec-butyl and tert-butyl), alkenyl (in particular C<sub>2-4</sub>-alkenyl, such as e.g. vinyl, 1-propenyl, 2-propenyl and butenyl), alkynyl (in particular C<sub>2-4</sub>-alkynyl, such as e.g. acetylenyl and propargyl) and aryl, in particular C<sub>6-10</sub>-aryl, such as e.g. phenyl and naphthyl), it being possible for the groups just mentioned optionally to contain one or more substituents, such as e.g. halogen and alkoxy. Methacryl and methacryloxypropyl radicals may also be mentioned in this connection.

In addition to the above examples of compounds of the formula I contained in the top layer composition, the following preferred examples may be mentioned for the compound (C):

CH<sub>3</sub>-SiCl<sub>3</sub>, CH<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>-SiCl<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,  
 C<sub>3</sub>H<sub>7</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,  
 (CH<sub>3</sub>O)<sub>3</sub>-Si-C<sub>3</sub>H<sub>6</sub>-Cl,  
 (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>, (CH<sub>3</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>,  
 (CH<sub>3</sub>)<sub>2</sub>Si(OH)<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub>, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OCH<sub>3</sub>)<sub>2</sub>,  
 (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, (i-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>SiOH,  
 CH<sub>2</sub>=CH-Si(OOCCH<sub>3</sub>)<sub>3</sub>,  
 CH<sub>2</sub>=CH-SiCl<sub>3</sub>, CH<sub>2</sub>=CH-Si(OCH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CH-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,  
 CH<sub>2</sub>=CH-Si(OC<sub>2</sub>H<sub>4</sub>OCH<sub>3</sub>)<sub>3</sub>, CH<sub>2</sub>=CH-CH<sub>2</sub>-Si(OCH<sub>3</sub>)<sub>3</sub>,  
 CH<sub>2</sub>=CH-CH<sub>2</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>,



- 5 Compounds of the type  $\text{SiR}_4$ , wherein the radicals R can be identical or different and represent a hydrolysable group, preferably an alkoxy group having 1 to 4 carbon atoms, in particular methoxy, ethoxy, n-propoxy, i-propoxy, n-butoxy, i-butoxy, sec-butoxy or tert-butoxy, are particularly preferably employed.

10

As can be seen, these compounds (C) (in particular the silicon compounds) also have non-hydrolysable radicals which contain a C-C double bond or triple bond. If such compounds are employed together with (or even instead of) the silicon compounds (A), monomers (preferably  
15 containing epoxide or hydroxyl groups) such as e.g. meth(acrylates) can also additionally be incorporated into the composition (these monomers can of course also have two or more functional groups of the same type, such as e.g. poly(meth)acrylates of organic polyols; the use of organic polyepoxides is also possible). In the case of curing of the corresponding  
20 composition induced by heat or photochemically, a polymerization of the organic species then takes place in addition to the build-up of the organically modified inorganic matrix, as a result of which the crosslinking density and therefore also the hardness of the corresponding coatings and shaped articles increases.

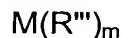
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Compound (C) is preferably employed in the composition for the scratch-resistant layer (SR) in an amount of 0.2 to 1.2 mol, based on 1 mol of silicon compound (A).

**Hydrolysable compound (D)**

The hydrolysable compound (D) is a compound of Ti, Zr or Al of the following general formula

5



wherein M represents Ti, Zr or Al and the radicals R''' can be identical or different and represent a hydrolysable group and n is 4 (M = Ti, Zr) or 3 (M = Al).

10

Examples of the hydrolysable groups are halogen (F, Cl, Br and I, in particular Cl and Br), alkoxy (in particular C<sub>1-6</sub>-alkoxy, such as e.g. methoxy, ethoxy, n-propoxy, i-propoxy and n-butoxy, i-butoxy, sec-butoxy or tert-butoxy, n-pentyloxy, n-hexyloxy), aryloxy (in particular C<sub>6-10</sub>-aryloxy, e.g. phenoxy), acyloxy (in particular C<sub>1-4</sub>-acyloxy, such as e.g. acetoxy and propionyloxy) and alkylcarbonyl (e.g. acetyl), or a C<sub>1-6</sub>-alkoxy-C<sub>2-3</sub>-alkyl group, i.e. a group derived from C<sub>1-6</sub>-alkylethylene glycol or -propylene glycol, wherein alkoxy has the same meaning as mentioned above.

20

Particularly preferably, M is aluminium and R''' is ethanolate, sec-butanolate, n-propanolate or n-butoxyethanolate.

Compound (D) is preferably employed in the composition for the scratch-resistant layer (SR) in an amount of 0.23 to 0.68 mol, based on 1 mol of the silicon compound (A).

25

A Lewis base (E) can additionally be used as a catalyst to achieve a more hydrophilic character of the scratch-resistant layer coating composition.

30

A hydrolysable silicon compound (F) with at least one non-hydrolysable radical which has 5 to 30 fluorine atoms bonded directly to carbon atoms, these carbon atoms being separated by at least 2 atoms of Si, can furthermore additionally be employed. The use of such a fluorinated silane  
5 leads to hydrophobic and soil-repellent properties additionally being imparted to the corresponding coating.

The preparation of the compositions for the scratch-resistant layer (SR) can be carried out by the process described in more detail below, in which  
10 a sol of the material (B) with a pH in the range from 2.0 to 6.5, preferably 2.5 to 4.0, is reacted with a mixture of the other components.

Even more preferably, they are prepared by a process, also defined below, in which the sol as defined above is added in two part portions to the  
15 mixture of (A) and (C), particular temperatures preferably being maintained, and the addition of (D) taking place between the two portions of (B), also preferably at a particular temperature.

The hydrolysable silicon compound (A) can optionally be prehydrolysed  
20 together with the compound (C) using an acid catalyst (preferably at room temperature) in aqueous solution, about 1/2 mol of water preferably being employed per mol of hydrolysable group. Hydrochloric acid is preferably employed as the catalyst for the prehydrolysis.

25 The particulate materials (B) are preferably suspended in water and the pH is adjusted to 2.0 to 6.5, preferably to 2.5 to 4.0. Hydrochloric acid is preferably used for the acidification. If boehmite is used as the particulate material (B), a clear sol forms under these conditions.

30 The compound (C) is mixed with the compound (A). The first part portion of the particulate material (B), suspended as described above, is then added. The amount is preferably chosen such that the water contained

therein is sufficient for semi-stoichiometric hydrolysis of the compounds (A) and (C). It is 10 to 70 wt.% of the total amount, preferably 20 to 50 wt.%.

- 5 The reaction proceeds slightly exothermically. After the first exothermic reaction has subsided, the temperature is adjusted by heating to approx. 28 to 35°C, preferably approx. 30 to 32°C, until the reaction starts and an internal temperature which is higher than 25°C, preferably higher than 30°C, and even more preferably higher than 35°C is reached. When the
- 10 addition of the first portion of the material (B) has ended, the temperature is maintained for a further 0.5 to 3 hours, preferably 1.5 to 2.5 hours, and the mixture is then cooled to approx. 0°C. The remaining material (B) is preferably added slowly at a temperature of 0°C. Thereafter, the compound (D) and optionally the Lewis base (E) are slowly added at
- 15 approx. 0°C, also preferably after the addition of the first part portion of the material (B). The temperature is then kept at approx. 0°C for 0.5 to 3 hours, preferably for 1.5 to 2.5 hours, before addition of the second portion of the material (B). Thereafter, the remaining material (B) is added slowly at a temperature of approx. 0°C. The solution added dropwise is preferably
- 20 precooled here to approx. 10°C directly before the addition into the reactor.

- After the slow addition of the second part portion of the compound (B) at approx. 0°C, the cooling is preferably removed so that the warming up of the reaction mixture to a temperature of more than 15°C (to room
- 25 temperature) takes place slowly, without additional heating.

- Inert solvents or solvent mixtures can optionally be added at any desired stage of the preparation in order to adjust the rheological properties of the scratch-resistant layer compositions. These solvents are preferably the
- 30 solvents already described above for the top layer composition.

The scratch-resistant layer compositions can comprise the conventional additives already described above for the top layer composition.

5 The application and curing of the scratch-resistant layer composition are carried out after surface-drying preferably by means of heat at 50 to 200°C, preferably 70 to 180°C, and in particular 110 to 130°C. Under these conditions the curing time should be less than 120, preferably less than 90, in particular less than 60 minutes.

10 The layer thickness of the cured scratch-resistant layer (SR) should be 0.5 to 30 µm, preferably 1 to 20 µm and in particular 2 to 10 µm.

The invention accordingly also provides a layer system comprising

- 15 (a) a substrate (S),
- (b) optionally a primer layer
- (c) a scratch-resistant layer (SR), as described above, and
- 20 (d) a top layer (T) formed from the composition prepared by the process according to the invention.

Any desired materials are possible as the substrate (S), in particular the

25 materials described above as substrates for the top layer (T). The substrate (S) is preferably mouldings, sheets and films of plastic, in particular based on polycarbonate.

The layer systems according to the invention can be prepared by a process which comprises at least the following steps:

5           (a)     application of the scratch-resistant layer coating composition to the substrate (S) and partial curing or polymerization of the coating composition under conditions such that groups which are still reactive are present.

10           (b)     application of the top layer coating composition according to the invention to the incompletely cured or polymerized scratch-resistant layer (SR) prepared in this way and curing thereof to form a top layer (T).

15           In the preparation of the layer systems it has proved to be particularly advantageous if the scratch-resistant layer (SR) is dried at a temperature of  $>110^{\circ}\text{C}$ , in particular  $110$  to  $130^{\circ}\text{C}$ , after the application. Excellent abrasion properties of the layer systems can be achieved by this means.

20           It is furthermore advantageous if the scratch-resistant layer coating composition comprises flow control agents in an amount of  $0.03$  to  $1$  wt. %.

25           It has furthermore proved to be particularly advantageous if the top layer coating composition is applied at a relative humidity of  $50$  to  $75\%$ , in particular  $55$  to  $70\%$ .

30           Finally, it has proved to be advantageous if the cured scratch-resistant layer (SR) is activated before application of the top layer coating composition. Possible activation processes are, preferably, corona treatment, flaming, plasma treatment or chemical etching. Flaming and corona treatment are particularly suitable. Reference is made to the embodiment examples in respect of the advantageous properties.



The present invention is more particularly described in the following examples, which are intended to be illustrative only, since numerous modifications and variations therein will be apparent to those skilled in the art. Unless otherwise specified, all parts and percentages are by weight.

5

### Examples

#### **Preparation of the coating composition for the scratch-resistant layer (SR)**

10

##### Example 1

354.5 g (3.0 mol) n-butoxyethanol were added dropwise to 246.3 g (1.0 mol) aluminium tri-sec-butanolate while stirring, during which the temperature rose to approx. 45°C. After cooling, the aluminate solution must be stored in a closed container.

1,239 g 0.1 N HCl were initially introduced into the reaction vessel. 123.9 g (1.92 mol) Böhmit Dispersal Sol P3<sup>®</sup> were added, while stirring. The mixture was then stirred for 1 hour at room temperature. The solution was filtered through a deep filter to separate off solid impurities.

787.8 g (3.33 mol) GPTS ( $\gamma$ -glycidyloxypropyltrimethoxysilane) and 608.3 g TEOS (tetraethoxysilane) (2.92 mol) were mixed and stirred for 10 minutes. 214.6 g of the boehmite sol were added to this mixture in the course of approx. 2 minutes. A few minutes after the addition the sol heated up to approx. 28 to 30°C and was also clear after approx. 20 minutes. The mixture was then stirred for approx. 2 hours at 35°C and then cooled to approx. 0°C.

600.8 g of the  $\text{Al}(\text{OEtOBu})_3$  solution in sec-butanol prepared as described above, containing 1.0 mol  $\text{Al}(\text{OEtOBu})_3$ , were then added at  $0^\circ\text{C} \pm 2^\circ\text{C}$ . When the addition had ended, the mixture was stirred for a further 2 hours at approx.  $0^\circ\text{C}$  and the remaining boehmite sol was then also added at  $0^\circ\text{C} \pm 2^\circ\text{C}$ . Warming of the reaction mixture obtained to room temperature without heating then took place in the course of approx. 3 hours. Byk 306<sup>®</sup> was added as a flow control agent. The mixture was filtered and the paint obtained was stored at  $+4^\circ\text{C}$ .

## 10 Example 2

### **Preparation of the coating composition**

GPTS and TEOS are initially introduced into the reaction vessel and mixed. The amount of boehmite dispersion (prepared analogously to example 1) necessary for semi-stoichiometric prehydrolysis of the silanes is slowly poured in, while stirring. The reaction mixture is then stirred for 2 hours at room temperature. The solution is then cooled to  $0^\circ\text{C}$  with the aid of a thermostat. Aluminium tributoxyethanolate is subsequently added dropwise via a dropping funnel. After addition of the aluminate, the mixture is stirred for a further 1 hour at  $0^\circ\text{C}$ . Thereafter, the remainder of the boehmite dispersion is added under thermostat cooling. After stirring for 15 minutes at room temperature, the cerium dioxide dispersion and BYK 306<sup>®</sup>, as a flow control agent, are added.

25

**Batch amounts:**

TEOS	62.50 g (0.3 mol)
DMDMS	-
GPTS	263.34 g (1 mol)
Boehmite	5.53 g (2 wt.%, based on the total solids)
0.1 N Hydrochloric acid	59.18 g
Cerium dioxide dispersion (20 wt.% in 2.5 wt.% acetic acid)	257.14 g (20 wt.%, based on the total solids)
Boehmite dispersion for semi-stoichiometric prehydrolysis	41.38 g
Aluminium tributoxyethanolate	113.57 g (0.3 mol)

**Preparation of the coating composition for the top layer (T)**

5

**Example 3**

A mixture of 130.0 g 2-propanol, 146,6 g distilled water and 2.8 g 37% hydrochloric acid was rapidly added dropwise to a mixture of 200.0 g TEOS and 20.0 g GPTS in 130.0 g 2-propanol. An exothermic reaction occurs, which is assisted by heating to 30 to 40°C. The reaction product is then cooled to room temperature and stirred for 1.5 hours. The coating sol obtained is stored under cool conditions at + 4°C. Before use, this concentrate is diluted with isopropanol to a solids content of 1,0 wt.% and 1.0 wt.% of the flow control agent BYK 347 (based on the solids content) is added.

10

15

### Preparation of the scratch-resistant coating systems

Test pieces were obtained as follows with the coating compositions obtained:

5

Sheets of polycarbonate based on bisphenol A ( $T_g = 147^\circ\text{C}$ ,  $M_w 27,500$ ) of dimensions  $105 \times 150 \times 4$  mm were cleaned with isopropanol and primed by flow-coating with a primer solution of 6 parts Araldite PZ 3962 and 1.32 parts Araldite PZ 3980 in 139.88 g diacetone alcohol according to the patent application PCT/EP01/03809 with subsequent heat treatment at  $130^\circ\text{C}$  for half an hour.

15 The primed polycarbonate sheets were then flow-coated with the base coat coating composition (example 1 or 2). The air-drying time for dust drying was 30 minutes at  $23^\circ\text{C}$  and 63% relative atmospheric humidity. The dust-dry sheets were heated in an oven at  $130^\circ\text{C}$  for 30 minutes and then cooled to room temperature.

20 Thereafter, the top layer coating composition (example 3) was applied, also by flow-coating. The wet film was air-dried for 30 minutes at  $23^\circ\text{C}$  and 63% relative atmospheric humidity and the sheets were then heated at  $130^\circ\text{C}$  for 120 minutes.

25 A surface activation of the cured scratch-resistant layer by flaming, corona treatment, plasma activation or chemical etching etc. proved particularly favourable for improving the adhesion and the flow of the top coat coating composition.

30 The application parameters such as temperature, time, humidity, layer thickness, application process and the content and type of flow control agent used were furthermore varied for comparison.

After curing had taken place the coated sheets were stored for two days at room temperature and then subjected to the following defined tests.

5 The properties of the coatings obtained with these paints were determined as follows:

- Cross-hatch test: EN ISO 2409:1994
- Cross-hatch test after storage in water: 65°C, tt = 0/0

10 The coated sheets are provided with a cross-hatch according to EN ISO 2409:1994 and stored in hot water of 65°C. The storage time (days) from which the first loss of adhesion in the tape test from 0 to 2 occurs is recorded.

- 15 - Taber Abraser test: Abrasion test DIN 52 347; (1,000 cycles, CS10F, 500 g)

The results of the evaluation are shown in tables 1 to 9.

20 Table 1 shows the abrasion (Taber values) and adhesion properties (cross-hatch test) of the layer systems prepared. The results show that the layer systems finished with the top layer (T) prepared according to the invention (examples 4 and 5) have considerably better abrasion and adhesion properties than those which comprise no top layer (T)

25 (comparison examples 6 and 7).

**Table 1**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Taber Abraser test hazing (%)	Cross-hatch test after storage in water (days)
Example 4	Example 1	Example 3	0.2	> 14
Example 5	Example 2	Example 3	1.5	> 14
Comparison Example 6	Example 1	none	0.9	14
Comparison Example 7	Example 2	none	4.4	7

The wetting and flow properties of the top layer coating composition on application to the scratch-resistant layer (SR) and the abrasion properties (Taber values) of the layer systems resulting therefrom as a function of the amount of flow control agent contained in the scratch-resistant layer coating composition are shown in table 2. The results show that particularly good wetting and abrasion value are achieved if the scratch-resistant layer coating composition comprises the flow control agent BYK 306 in an amount of 0.05 to 0.2 wt. %.

**Table 2**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Flow control agent BYK 306 (wt.%) in the base coat	Wetting/ flow of the top layer	Taber Abraser test hazing (%)
Example 8	Example 2	Example 3	0.1	good	1.5
Example 9	Example 2	Example 3	0.3	good	3.4 and partial rubbing off
Example 10	Example 2	Example 3	0.03	inadequate	n.d.

Table 3 shows the abrasion properties (Taber values) of the layer systems as a function of the stoving time and temperature of the scratch-resistant layer (SR). The results show that the increase in the stoving temperature to values greater than 110°C is accompanied by an improvement in the

5 Taber values.

**Table 3**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Stoving temperature after application of the scratch-resistant layer (°C)	Stoving time after application of the scratch-resistant layer (min)	Taber Abraser test hazing (%)
Example 11	Example 2	Example 3	130	30	1.5
Example 12	Example 2	Example 3	130	60	partial rubbing off of the top layer
Example 13	Example 2	Example 3	120	30	1.7
Example 14	Example 2	Example 3	110	30	2.0
Example 15	Example 2	Example 3	100	30	3.4

10 Table 4 shows the abrasion properties (Taber values) of the layer systems as a function of the solids content of the top layer (T). The results show that particularly good Taber values are achieved if the solids content in the top layer is 0.5 to 1.5 wt. %.

**Table 4**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Solids content of the top layer	Taber Abraser test hazing (%)	Observation
Example 16	Example 2	Example 3	1.0 %	1.5	OK
Example 17	Example 2	Example 3	2.0 %	4.1	cracking at the sheet edge
Example 18	Example 2	Example 3	3.0 %	3.5	cracking over the entire sheet

Table 5 shows the abrasion properties (Taber values) of the layer systems as a function of the type and amount of flexibilizing agent contained in the top layer coating composition. The flexibilizing agents employed were:

5 glycidyloxypropyltrimethoxysilane (GPTS), methyltriethoxysilane (MTS) and dimethyldimethoxysilane (DMDMS). The results show that particularly good Taber values can be achieved with GPTS or DMDMS in an amount of about 10 wt.% or MTS in an amount of about 20 wt.%.

10

**Table 5**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Flexibilizing agent in the top layer (T)		Taber Abraser test hazing (%)
			type	content (%)	
Example 19	Example 2	Example 3	GPTS	10	1.5
Example 20	Example 2	Example 3	GPTS	20	3.7
Example 21	Example 2	Example 3	GPTS	30	3.4
Example 22	Example 2	Example 3	MTS	10	2.3
Example 23	Example 2	Example 3	MTS	5	2.4
Example 24	Example 2	Example 3	MTS	20	1.3
Example 25	Example 2	Example 3	MTS	30	2.1
Example 26	Example 2	Example 3	DMDMS	5	4.5
Example 27	Example 2	Example 3	DMDMS	10	2.5
Example 28	Example 2	Example 3	DMDMS	20	3.8



The wetting and flow properties of the top layer coating composition on application to the scratch-resistant layer (SR) and the abrasion properties (Taber values) of the layer system resulting therefrom as a function of the amount of flow control agent contained in the top layer coating

- 5 composition are shown in table 6. The results show that by using the flow control agent BYK 347 or BYK 306 in an amount of at least 0.5 wt.%, in particular 1-10 wt.%, excellent Taber values coupled with simultaneously good wetting and flow properties are achieved.

10 **Table 6**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Flow control agent in the top layer (T)		Wetting/flow	Taber Abraser test hazing (%)
			type	content (%)		
Example 29	Example 2	Example 3	BYK 347	1.0	very good	1.5
Example 30	Example 2	Example 3	BYK 347	0.3	disturbances	3.2
Example 31	Example 2	Example 3	BYK 347	5.0	very good	1.7
Example 32	Example 2	Example 3	BYK 347	50.0	very good	2.3
Example 33	Example 2	Example 3	BYK 306	1.0	good	1.9
Example 34	Example 2	Example 3	BYK 306	0.3	disturbances	2.8
Example 35	Example 2	Example 3	BYK 306	5.0	very good	2.1
Example 36	Example 2	Example 3	BYK 306	50.0	very good	2.7

- 15 Table 7 shows various physical properties of the layer systems as a function of the relative humidity on application of the top layer coating composition to the scratch-resistant layer (SR). The results show that a particularly good profile of properties is obtained if the application of the top layer (T) is carried out at a relative humidity of 50 to 75%, in particular 55 to 70%.

**Table 7**

Layer system	Scratch-resistant layer (SR)	Top layer (T)	Relative humidity during application (%)	Hazing of the scratch-resistant layer	Cracking of the paint layer	Taber Abraser test hazing (%)	Appearance of the top layer
Example 37	Example 2	Example 3	63	none	none	1.5	OK
Example 38	Example 2	Example 3	30	none	slight	14.0	rubbed through
Example 39	Example 2	Example 3	40	none	slight	-	partly rubbed through
Example 40	Example 2	Example 3	51	none	slight	2.7	partly rubbed through
Example 41	Example 2	Example 3	73	yes	none	n.d.	n.d.

The wetting and flow properties of the top layer coating composition on application to the scratch-resistant layer (SR) and the abrasion properties (Taber values) of the layer systems resulting therefrom as a function of the surface treatment (activation) of the scratch-resistant layer (SR) are shown in table 8. In examples 42 and 43 the scratch-resistant layer is as example 2, cured at 130°C for 60 minutes, and the top layer is as example 3, but with 0.3% BYK 306 as the flow control agent. The application was carried out at 23°C and 40% relative humidity. In examples 44, 45 and 46 the scratch-resistant layer is as example 2, cured at 130°C for 60 minutes, and the top layer is as example 3, but with 0.3% BYK 306 as the flow control agent. The application was carried out at 23°C and 62 % relative humidity. The results show that the wetting and abrasion properties are improved considerably by corona treatment or flaming of the scratch-resistant layer before application of the top layer.

**Table 8**

Layer system	Activation before application of the top layer	Surface tension of the scratch-resistant layer after activation (mN/m)	Wetting by the top layer coating composition	Taber Abraser test hazing (%)
Example 42	none	33.6	moderate	8.6 top layer rubbed through
Example 43	by corona treatment	45.3	good	3.2 partly rubbed through
Example 44	none	35.7	moderate	7.5 top layer rubbed through
Example 45	single flaming	49.9	good	3.6 partly rubbed through
Example 46	flaming twice	64.8	very good	2.2 OK

#### **Storage stability (pot life) of the top layer coating composition**

- 5 The storage stability (pot life) of the top layer coating composition prepared according to example 3 by joint hydrolysis was compared with the coating sol prepared according to example 2 of the laid-open specification DE 199 52 040 A1 by separate hydrolysis. The abrasion properties (Taber values) of the layer systems prepared with the two
- 10 coating compositions were furthermore compared with one another. The preparation of the scratch-resistant layer and the application were carried out according to example 5.

**Table 9**

Storage age of the sols at 4°C	Taber Abraser test hazing (%)	
	Top layer according to Example 3	Top layer according to example 2 of DE 199 52 040 A1 (comparison example)
1 day	1.4	1.6
4 weeks	1.5	2.9 partly rubbed through
12 weeks	1.4	6.5 rubbed through, difficult coating

5 The results show that the top layer coating compositions prepared by the process according to the invention have a considerably improved storage stability (pot life) compared with the top layer coating composition prepared according to DE 199 52 040 A1. The results furthermore show that layer systems with the top layer coating compositions prepared by the process according to the invention have improved abrasion properties (Taber values) compared with DE 199 52 040 A1.

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Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may  
15 be limited by the claims.